

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



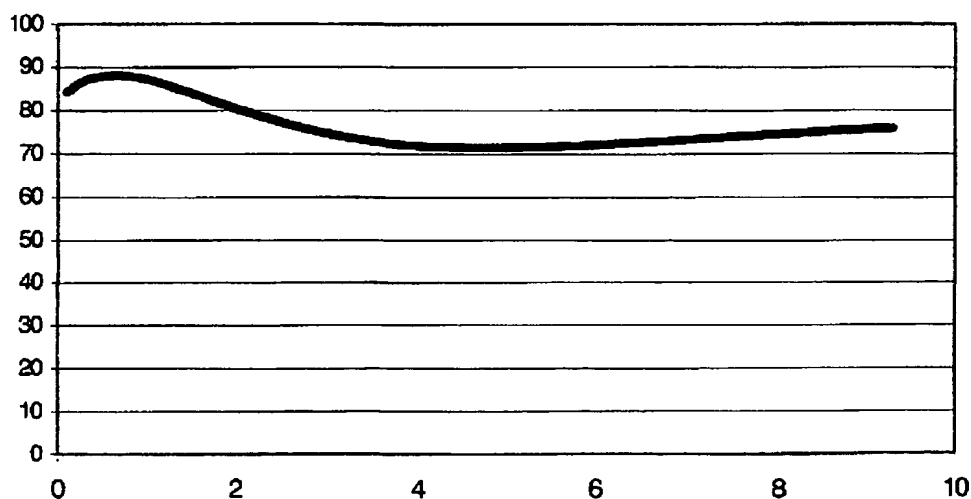
(43) International Publication Date  
27 June 2002 (27.06.2002)

PCT

(10) International Publication Number  
**WO 02/50012 A1**

- (51) International Patent Classification<sup>7</sup>: C07C 51/48, 51/265, B01D 61/04
- (21) International Application Number: PCT/IB01/02331
- (22) International Filing Date: 6 December 2001 (06.12.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/257,974 21 December 2000 (21.12.2000) US
- (71) Applicant (for all designated States except US): INCA INTERNATIONAL S.P.A. [IT/IT]; Via Patrocolo, 21, I-20151 Milan (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): PIRAS, Luciano [IT/IT]; Via Roberto Bellarmino, 1, I-20141 Milan (IT). SORO, Luigi [IT/IT]; Via Enrico Berlinguer, I-09074 Ghiarza (IT). CHIARELLI, Michelle [IT/IT]; Via Cirano, 35, I-27015 Landriano (IT). LANARI, Francesco [IT/IT]; Via Pascoli, 19/1, I-20059 Vimercate (IT).
- (54) Agent: VON CUNOW, Dorothee; Dow Europe S.A., Intellectual Property Section, Bachtobelstrasse 3, CH-8810 Horgen (CH).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: USE OF OSMOTIC MEMBRANES IN TEREHPHTHALIC ACID PRODUCTION



(57) Abstract: The use of reverse osmotic membranes to remove some acetic acid from the aqueous acetic acid streams which are generated in the terephthalic acid production is disclosed. The use of these membranes provides a more energy efficient and less capital-intensive method for purifying aqueous streams and obtaining acetic acid for recycling back into the production process.

WO 02/50012 A1

## USE OF OSMOTIC MEMBRANES IN TEREPHTHALIC ACID PRODUCTION

5 The present invention relates to a new process for the production of crude terephthalic acid ("CTA"). More particularly, this application relates to the use of reverse osmotic membranes to remove some acetic acid from the aqueous acetic acid streams, which are generated in the CTA production.

10 Crude Terephthalic Acid is produced by direct oxidation of p-xylene using acetic acid as solvent and subsequent crystallization from the mother liquor to recover the Crude Terephthalic Acid (CTA). The slurry from the crystallizers is fed to a filtration device in which the CTA is separated from its mother liquor. To clean out the crystals from mother  
15 liquor residues the CTA is washed, typically into the same filtering device, with recovered acetic acid. The CTA is then dried and stored in storage silos to feed the purification section.

The typical process for CTA production and solvent recovery involves, among others, the steps of:

1. Mixing the p-xylene with acetic acid
2. Oxidizing the p-xylene using a source of molecular oxygen
3. Crystallizing the solid from its mother liquor and wash-  
25 ing the solid so recovered with solvent, to eliminate the residual mother liquor
4. drying the washed solid in a suitable dryer
5. storing the dry solid in storage silos
6. washing almost all off gas streams with acetic acid  
30 and/or water
7. Collecting all the streams containing acetic acid and directing the streams to a distillation section to separate acetic acid to be recycled from water, to be recy-

clad or directed to a wastewater treatment plant. Typically the acetic acid so recovered contains from 1 to 6 percent wt of water, while the distilled water typically contains from 0.01 to 2 percent wt of acetic acid.

5 In order to reduce the cost connected to the treatment the water must meet certain purity standards. These purity standards typically require the use of large distillation towers in order to minimize the levels of acetic acid or other impurities contained in the water. These larger, more  
10 elaborate columns are also more costly, both in terms of capital and in terms of energy cost required to operate them. These energy requirements for operating such columns increase with greater amounts of water present in the acetic acid. Accordingly, it would be beneficial to develop a more cost-  
15 effective way to remove the water.

Osmotic membranes are well known in the art for use in purification of liquids. In reverse osmosis, the aqueous solution is forced against an osmotic membrane (that is, a water-permeable membrane capable of selectively passing water  
20 through the membrane). In this process the flow of water under the applied hydrostatic pressure is in a direction opposite to that normally observed in direct osmosis. When the pressure of the aqueous solution exceeds the osmotic pressure of the impurity, water is preferentially forced through the  
25 membrane, effectively lowering the concentration of the impurity on that side of the membrane. Additional osmotic membranes in series may further treat this more pure stream until the purity of the water passing through the membrane is at a desired level.

30 Applicants have discovered that osmotic membranes can be advantageously used to remove some of the water from the aqueous acetic acid streams in a CTA production plant. The use of these osmotic membranes can lead to significant cost reductions, especially when used in conjunction with distil-

lation towers, albeit smaller columns than previously required.

The present invention involves the use of one or more osmotic membranes to remove at least a portion of the acetic acid from the water in at least one of the aqueous acetic acid streams produced in a terephthalic acid production facility. The osmotic membrane can be any membrane known in the art, which is capable to some extent of selectively passing water through the membrane while retaining acetic acid behind. It is preferred that the membrane also provides retention of other impurities which are commonly seen in the aqueous acetic acid streams, such as for example p-xylene or methyl acetate. The spiral-wound elements membranes are most preferred.

The osmotic membranes used in the present invention can be installed in any aqueous acetic acid stream. Because of the pressure limitations of most commercially available membranes, the stream practically should contain no more than 25 percent by weight acetic acid. This corresponds to an approximate osmotic pressure of 70 bar, which is the burst limit of most commercial membranes. Accordingly it is preferred that the osmotic membranes be installed in streams having 25 percent or less acetic acid content.

As it is known in the art, an osmotic membrane has certain efficiency for retaining the impurities (such as acetic acid), such that some impurities will almost always pass through the membrane. For this reason it is preferred that a series of membranes be used sequentially such that the purified stream from a first membrane is passed to a second membrane. The purified stream from that second membrane can then be passed to a third membrane and so on until the final stream is sufficiently pure.

Simultaneously, the stream of (now less concentrated) aqueous acetic acid, which did not pass through one of the membranes, can be routed as input to another membrane or a series of membranes in the sequence in accordance with the

limitation connected to the relevant osmotic pressure. In this way an aqueous stream with a higher concentration of acetic acid is obtained, along with an aqueous stream which is less concentrated in acetic acid (and other impurities).

5 When the desired concentration is reached in the more concentrated stream, it is preferably routed to a distillation section, as it is herein described.

The number of sequential membranes depends on the efficiency of the membranes in removing the impurities, as it is  
10 known in the art. Similarly, the routing of the various streams through the various membranes can be optimized and controlled (preferably electronically) according to methods known in the art.

As is known in the art, most of the water from the concentrated stream can be removed by distillation. As earlier  
15 indicated the stream coming from the membrane(s), which is concentrated in acetic acid, is preferably directed to a distillation section.

The required energy to run a distillation section in a plant of terephthalic acid is known in the art. The use of  
20 osmotic membranes jointly with a distillation section is economically advantageous in comparison with the single distillation section itself. In fact, by combining the two systems, the osmotic membranes and the distillation, the total  
25 amount of energy required to separate the acetic acid from the water is less and the investment costs are lower, because the resulting distillation section can be smaller. It is also contemplated that by using the osmotic membranes for the final purification, either the reflux ratio or the number of  
30 stages of the distillation tower, that separates acetic acid from water, can be significantly reduced.

The concentrated acetic acid is collected in the bottom of the tower and reused in the process. The water is collected in the top of the tower and can be recycled, disposed  
35 of, or most preferably routed to the osmotic membrane (or at a suitable stage within the sequence of osmotic membranes)

for further purification if needed. It is generally preferred that the purified water stream coming from the final membrane contains less than 0.01 percent by weight acetic acid, although local conditions will dictate the actual need.

5 Obtaining purity levels this high through distillation alone would require large amounts of energy and much larger distillation columns. This water can be recycled for reuse in the various washes used in a typical terephthalic acid plant or be routed to disposal.

10 It is contemplated that the membranes can be used to purify the aqueous acetic acid streams coming from several process streams. Ideally when membranes are used sequentially, the various streams are routed to the appropriate membrane such that it closely matches the concentration of the streams  
15 entering the membrane.

As is known in the art, the presence of solids can hinder the performance of osmotic membranes. Accordingly if a particular stream contains solids, it may be desirable to remove the solids prior to sending the streams to the membranes. Suitable devices for filtering or otherwise removing  
20 the solids are well known in the art. Shown in Figure 1 are the typical values of the efficiency of the osmotic membranes, observed while separating water from acetic acid, on the basis of a single pass through the membrane. On the x  
25 axis are reported the concentrations of acetic acid in a water solution such as those observed in a process stream before the separation; on the y axis are displayed the amount of acetic acid removed from the stream as a percentage of the initial feed concentration. This figure demonstrates that it  
30 is possible to remove acetic acid from aqueous streams using osmotic membranes.

CLAIMS:

1. A process for producing terephthalic acid wherein one or more aqueous acetic acid streams are produced, in which an osmotic membrane system comprising one or more os-  
5 motic membranes is used to remove at least a portion of the acetic acid from the water in at least one of the streams.

2. The process of Claim 1 wherein the acetic acid content in the water stream leaving the osmotic membrane system is lower than 1 percent by weight

10 3. The process of Claim 1 wherein the acetic acid been removed from the water by the osmotic membrane system is re-used as solvent in the terephthalic acid production.

4. The process of Claim 1 further comprising the step of performing a separation of the acetic acid and water using  
15 a distillation tower prior to removing additional acetic acid from the water stream using the osmotic membrane system.

5. The process of Claim 4 wherein the water stream coming from the distillation tower contains less than 25 percent by weight of acetic acid.

20 6. The process of Claim 5 wherein the acetic acid that has been removed from the water stream using the osmotic membrane system is recycled back to the distillation tower.

7. The process of Claim 1 wherein the osmotic membrane used in the system is selected from the group comprising the  
25 whole SW family of FILMTEC Corporation.

8. The process of Claim 1 wherein solids are removed from one or more streams before being sent to the osmotic membrane system.

9. The process of Claim 8 wherein the stream(s) is  
30 filtered to remove solids prior to sending it to the osmotic membranes system.

10. The process of Claim 1 wherein the aqueous acetic acid stream further contains p-xylene and/or methyl acetate and wherein the osmotic membrane system also separates at

least a portion of the p-xylene and/or methyl acetate from the water.

11. The process of Claim 1, wherein the osmotic membrane system comprises more than one osmotic membrane arranged sequentially.

12. The process of Claim 11 wherein more than one aqueous acetic acid streams are produced, and wherein each particular aqueous acetic acid stream is directed to the osmotic membrane system at a location in which the acetic acid content of the particular aqueous acetic acid stream most closely matches the acetic acid content in the osmotic membrane system.



FIG. 1

# INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/IB 01/02331

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C51/48 C07C51/265 B01D61/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 855 491 A (CHEW CALVIN T ET AL) 8 August 1989 (1989-08-08) column 1, line 8 - line 14 column 2, line 22 - line 45 column 2, line 66 - column 3, line 10 column 3, line 32 - line 45 claim 1	1-12
X	US 5 635 071 A (AL-SAMADI RIAD A) 3 June 1997 (1997-06-03) column 1, line 4 - line 9 column 3, line 17 - column 4, line 21 column 8, line 15 - column 11, line 27	1-12
X	US 5 492 625 A (WYTCHERLEY RANDA W ET AL) 20 February 1996 (1996-02-20) column 1, line 37 - column 2, line 33	1-12
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

3 April 2002

Date of mailing of the international search report

12/04/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

O'Sullivan, P

## INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/IB 01/02331

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 652 203 A (GLITSCH) 10 May 1995 (1995-05-10) column 1, line 31 - line 47 column 2, line 14 - line 24 claim 1 -----	1-12
A	EP 1 018 489 A (NIPPON CATALYTIC CHEM IND) 12 July 2000 (2000-07-12) column 1, line 3 - line 18 column 2, line 17 - line 46 column 4, line 6 - line 11 -----	1-12
A	WO 98 41478 A (JEFFERY IAN CHARLES ;JACKSON CHRISTOPHER HOWARD (GB); DU PONT (US)) 24 September 1998 (1998-09-24) page 1, line 1 - line 20 -----	1-12

INTERNATIONAL SEARCH REPORT  
Information on patent family members

Int. application No.  
PCT/IB 01/02331

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4855491	A	08-08-1989	NONE	
US 5635071	A	03-06-1997	NONE	
US 5492625	A	20-02-1996	AU 685496 B2 AU 7573394 A BR 9501499 A CA 2117595 A1 CN 1117040 A CZ 9500846 A3 DE 69414523 D1 DE 69414523 T2 EP 0652203 A1 ES 2123720 T3 HU 71997 A2 JP 2676681 B2 JP 8040972 A SK 43295 A3 US 5624566 A ZA 9502622 A	22-01-1998 18-05-1995 07-11-1995 08-10-1995 21-02-1996 15-11-1995 17-12-1998 08-04-1999 10-05-1995 16-01-1999 28-03-1996 17-11-1997 13-02-1996 11-10-1995 29-04-1997 14-12-1995
EP 0652203	A	10-05-1995	US 5492625 A US 5399751 A AU 685496 B2 AU 7573394 A BR 9501499 A CA 2117595 A1 CN 1117040 A CZ 9500846 A3 DE 69414523 D1 DE 69414523 T2 EP 0652203 A1 ES 2123720 T3 HU 71997 A2 JP 2676681 B2 JP 8040972 A SK 43295 A3 US 5624566 A ZA 9502622 A CZ 9402351 A3 HU 72347 A2 SK 120094 A3	20-02-1996 21-03-1995 22-01-1998 18-05-1995 07-11-1995 08-10-1995 21-02-1996 15-11-1995 17-12-1998 08-04-1999 10-05-1995 16-01-1999 28-03-1996 17-11-1997 13-02-1996 11-10-1995 29-04-1997 14-12-1995 16-08-1995 29-04-1996 07-06-1995
EP 1018489	A	12-07-2000	EP 1018489 A2 JP 2000254644 A JP 2000254669 A	12-07-2000 19-09-2000 19-09-2000
WO 9841478	A	24-09-1998	AU 6509398 A BR 9815459 A CN 1250428 T DE 69801423 D1 EP 0966405 A1 ES 2162428 T3 WO 9841478 A1 TR 9902222 T2 US 6254779 B1 ZA 9802020 A	12-10-1998 16-10-2001 12-04-2000 27-09-2001 29-12-1999 16-12-2001 24-09-1998 21-02-2000 03-07-2001 14-09-1998